U.S. Department of Energy

Office of River Protection

BECHTEL

JUL 15 2003

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03-ED-111

Mr. Michael A. Wilson, Program Manager
Nuclear Waste Program
State of Washington
Department of Ecology
1315 W. Fourth Avenue
Kennewick, Washington 99336

RECEIVED
SEP 19 2003
EDMC

Dear Mr. Wilson:

REQUEST TO DELETE PERMIT CONDITION III.10.C.14

Reference: WA7890008967, "Dangerous Waste Portion of the Hanford Facility Resource Conservation and Recovery Act Permit for the Treatment, Storage, and Disposal of Dangerous Waste, Chapter 10 and Attachment 51, 'Waste Treatment and Immobilization Plant.'"

This letter transmits a permit modification request for the State of Washington Department of Ecology review and approval to delete Permit Condition III.10.C.14 from the referenced permit.

Permit Condition III.10.C.14 requires a testing program be performed to determine destruction and removal efficiency of organic spikes in a pilot-scale melter and to determine if the operational melters would be damaged by using simulant with high levels of organic compounds.

Destruction and removal efficiencies for the pilot-scale melter and preliminary test results obtained indicate that the concentrations of recommended spike organics will not affect the operational life of the melters. After related discussions with your permitting staff, a dangerous waste modification package to remove the pilot-scale testing permit condition is attached.

Richland Operations Office
P.O. Box 550
Richland, Washington 99352

Office of River Protection
P.O. Box 450
Richland, Washington 99352

Bechtel National, Inc.
2435 Stevens Center Place
Richland, Washington 99352

If you have any questions, please contact Lori A. Huffman, Office of River Protection, Environmental Division, (509) 376-0104.

James E. Rasmussen, Director
Environmental Division
Office of River Protection

Joel Hebdon, Director
Regulatory Compliance and Analysis Division
Richland Operations Office

J. P. Henschel, Project Director
Bechtel National, Inc.

Attachment

cc w/attach:
B. Erlandson, BNI
J. P. Henschel, BNI
J. Cox, CTUIR
S. Dahl-Crumpler, Ecology
S. J. Skurla, Ecology
S. A. Thompson, FHI
P. Sobotta, NPT
J. B. Hebdon, RL (w/o attach)
A. C. McKarns, RL
R. Jim, YN
Administrative Record
Environmental Portal, LMSI

Attachment
03-ED-111

Basis for Deletion of Pilot-Scale Melter Testing from the Dangerous Waste Permit

Hanford Facility RCRA Permit Modification Notification Form

Part III, Chapter 10 and Attachment 51

Waste Treatment and Immobilization Plant

July 15, 2003

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Hanford Facility RCRA Permit Modification Notification Form	
Unit: **Waste Treatment and Immobilization Plant**	Permit Part & Chapter: **Part III, Chapter 10 and Attachment 51**

Description of Modification: Delete III.10.C.14. Performance Test Demonstration
Attachment 51, Chapter : 10
Redline/strikeout of modification

III.10.C.14. ~~Performance Test Demonstrations~~ Reserved.

~~The performance test program will demonstrate that the melter and melter off-gas systems are capable of 99.99% Destruction Removal Efficiency (DRE) for organics pursuant to Permit Conditions III.10.H.1.b.i. and III.10.J.1.b.i. The test program will include analyses and a demonstration with a pilot scale melter using high concentrations (above rated design limits) of organic spikes in order to obtain detectable output concentrations upon which to determine DRE. The pilot scale performance test plan will be submitted by the Permittees to Ecology by January 31, 2004. Ecology approval of the of the pilot scale melter test plan is expected by March 31, 2004. Demonstration of compliance with the 99.99% DRE listed in Permit Conditions III.10.H.1.b.i. and III.10.J.1.b.i. in the pilot scale melter shall be conducted in accordance with the approved pilot scale melter test plan and completed by November 15, 2004. If the test compromises the ability of the melter to continue operations due to high organic spikes, as defined by the approved pilot scale test performance test plan, then no further full scale, high organic demonstration testing on the WTP Unit melters shall be required. The testing of the installed, operational WTP Unit melters and off-gas systems will use pilot scale pilot melter test data and revised WTP Unit test parameters for the full scale demonstration test.~~

~~The pilot scale performance test plan will include the following information:~~

~~i. Discussion on how the pilot scale melter reasonably simulates operations in the LAW and HLW Vitrification Systems;~~

~~ii. Identification of high organic spikes test levels, spiking methods, and types of chemicals to be used for spiking;~~

~~iii. Definition of expected waste feed organic content (concentration and types), plus sugar content, plus organic spike content (concentration and types);~~

~~iv. Identification of proposed test conditions, including consideration of testing combined organics and metals, as well as separate metal and organic testing; and~~

~~v. Identification of the criteria for test success or failure and a discussion of how the results will be interpreted.~~

~~Results from the Test Report will be incorporated into the full scale demonstration test.~~

Basis for the deletion of Permit Condition III.10.C.14, Performance Test Demonstration, is attached.

Modification Class: [1] [2] [3] Please check one of the Classes:	Class 1	Class [1]1	Class 2	Class 3
				X

Relevant WAC 173-303-830, Appendix I Modification: A.5.a, General Permit Provisions

Enter wording of the modification from WAC 173-303-830, Appendix I citation
Request downgrade to Class [1]1.

Submitted by Co-Operator:	Reviewed by ORP:	Reviewed by Ecology:	Reviewed by Ecology:
J. P. Henschel Date 7/11/03	W. J. Taylor Date 7/11/03	S. Dahl-Crumpler Date	L. Ruud Date

Basis for Deletion of Pilot-Scale Melter Testing from the Dangerous Waste Permit

Introduction

The Waste Treatment and Immobilization Plant (WTP) Project is required by regulatory permit conditions to perform pilot-scale performance testing to determine whether such testing could affect the operational life of the WTP melters. Research and Testing (R&T) test results obtained since the establishment of this permit condition demonstrate that the concentrations of recommended spike organics will not affect the operational life of the WTP melters.

Background

Reference 1 describes the current WTP requirement for compliance testing. Section III.10.C.14, Performance Test Demonstrations, states; "The performance test program will demonstrate that the melter and melter off-gas systems are capable of 99.99% Destruction Removal Efficiency (DRE) for organics pursuant to Permit Conditions III.10.H.1.b.i. and III.10.J.1.b.i. The test program will include analyses and a demonstration with a pilot scale melter using high concentrations (above rated design limits) of organic spikes in order to obtain detectable output concentrations upon which to determine DRE. The pilot scale performance test plan will be submitted by the Permittees to Ecology by January 31, 2004. Ecology approval of the pilot scale melter test plan is expected by March 31, 2004. Demonstration of compliance with the 99.99% DRE listed in Permit Conditions III.10.H.1.b.i. and III.10.J.1.b.i. in the pilot scale melter shall be conducted in accordance with the approved pilot scale melter test plan and completed by November 15, 2004."

The bases for the pilot testing was WTP technical staff concern for possible risks to the plant melters from processing undefined quantities of organics (Reference 2) that could result in precipitation of reduced metals in the vitrification melters. In early 2002 the number of possible organics and the necessary feed concentrations required to demonstrate the required DRE, particularly candidate organics that are "easy to destruct," was not defined. As the melter feed is heated, the organics behave as reducing agents. Various fractions will evaporate, oxidize in the plenum space, and some will persist in the cold cap and react with oxidants, such as nitrate, in the feed; as well as the metals. Because of the large number of feed constituents and hard-to-predict thermal conditions in the cold cap, the extent of evaporation and reactions between organics and metals can not be predicted. Over-reduction of the melt will lead to the formation of metals and metal sulfides. As a result, empirical laboratory and pilot equipment testing have been performed to measure the effect of organics on glass redox state. The redox state of the glass is inferred by measuring the ratio of Fe^{+2}: Fe^{total} in the product glass. The maximum limit of this ratio is set at 0.3 to assure reduced metals and sulfides do not occur. These compounds fall to the melter floor where they can accelerate refractory corrosion ("downward drilling"). If sufficient material accumulates, power surging, localized overheating of glass, and electrical short circuiting of the electrodes can occur. The Low-Activity Waste (LAW) melter is much more susceptible to these effects than the High-Level Waste (HLW) melter because of the LAW melters' electrode design.

Subsequent to the initial assessment that a large concentration of organics may be required, organic selection will be based on selecting a limit number, i.e., up to three, hard-to-destroy organics based on the Dayton List or similar ranking system. The Environmental Protection Agency (EPA) has agreed to this approach for demonstrating DRE organic requirements in glass are met. WTP also developed a pilot-scale testing approach to utilize a limited number of test organics that are hard-to-destroy and would represent the categories of organics of concern from a risk assessment approach.

Review of Pertinent R&T Results

Pilot melter testing of LAW and HLW flowsheets in 2002 has provided a strong technical basis on which to reconsider the early WTP position. The following information is summarized from subcontractor vendor reports.

The concentration of the organic spikes required to demonstrate a certain DRE value is dependent on analytical detection limits, air sample size, volumetric air flow rates and feed rates. Most of these variables are fixed as a result of EPA method requirements or physical limitations of the melter system. Data from analytical procedures are typically reported with respect to method detection limits (MDL) and estimated quantitation limits (EQL), which can be anywhere from five to 50 times higher. For pilot testing of simulated LAW and HLW melter feeds, detection limits were selected for the purpose of DRE calculations based on previous experience, consultation with various vendors, and SW-846 methods. For testing purposes, expectations were that the spike levels should be sufficient to determine a DRE of 99.999%. Off-gas system flow rates and melter feed rates determined during initial testing provided the basis for organic spiking used in subsequent testing.

Example calculation results to estimate the amounts of spike organics required for pilot testing are provided below. Note that the MDLs are used as the basis for calculation in these examples but the EQLs (which are typically about a factor of ten higher) can be easily substituted.

Assumptions:

- DM1200 air flow rate of 5 dry standard cubic meter(dscm)/minute (min) into the thermal catalytic oxidizer;
- DM1200 melter feed rate of 118 liters (L) per hour (hr)
  Volatiles (chlorobenzene, trichloroethene);
- Air: 0.1 μg/dscm (MDL) × 5 dscm/min (estimated air flow rate) = 0.0005 milligrams (mg)/min;
- Feed concentration to establish DRE of 99.999%: 50 mg/min × 60 min/hr / 118 liter/hr = 25 mg/liter
  Semi Volatiles (naphthalene);
- Air: 1 μg/dscm (MDL) × 5 dscm/min (estimated air flow rate) = 0.005 mg/min; and
- Feed concentration to establish DRE of 99.999%: 500 mg/min × 60 min/hr / 118 liter/hr = 255 mg/liter.

Physical and Chemical Property Data of Test Organics (Reference 7):

Chlorobenzene: C_6H_5Cl; molecular weight (mol. wt). 112.56; 62.04% Carbon; specific gravity. 1.107; boiling point. 131-132°C; flash point. 28°C
Trichloroethylene: $ClCH=CCl_2$; mol. wt. 131.40; 18.28% Carbon; specific gravity. 1.4649; boiling point. 86.7°C
Naphthalene: $C_{10}H_8$; mol. wt. 128.16; 93.71% Carbon; specific gravity. 1.162; melting point. 80.2°C; boiling point. 218°C; flash point. 28°C

A similar estimation has been made for the LAW and HLW melter systems based also on MDL measurement requirements (Reference 3). Each HLW melter has dedicated primary and secondary off-gas treatment systems. Each LAW melter has a dedicated primary and shared secondary off-gas treatment system. For the three Metric Tons of Glass per day (MTG/day) Immobilized High-Level Waste (IHLW) throughput production case it, was estimated that Volatile Organic Chemicals (VOC) spike organics would be required at a melter feed concentration of 78 mg/L. Semivolatile Organic Chemicals (SVOC) spike organics would be required at a melter feed concentration of 780 mg/L. For Immobilized Low-Activity Waste throughput production at 30 MTG/day VOC and SVOC organic spike levels would be 33 mg/L and 333 mg/L, respectively. If a LAW facility performance demonstration were to be conducted with one melter only, these concentrations would be adjusted depending on the total flow to the secondary off-gas treatment.

Testing conducted in 2002 is reported in References 4, 5 and 6. Following the estimation of minimum required mass flux of organic spike chemicals and preliminary testing, Vitreous State Laboratory (VSL) elected to increase the quantities of volatile organic spike chemicals by over 30X to account for any process variability or miscalculations. The actual concentrations tested in the DM1200 pilot melter (DM1200), along with the projected WTP test requirements (Reference 3) are presented in the tables below. Testing is performed on the DM1200 because this pilot test facility includes prototypic primary and secondary off-gas treatment equipment.

Test Organic	LAW Melter Feed Concentration, mg/L				HLW Melter Feed Concentration, mg/L	
	DM1200			WTP[1]	DM 1200[2]	WTP
	C1	A1	B1			
Chlorobenzene	918	793	231	33	354	78
Trichloroethylene	1221	1054	306	33	469	78
Naphthalene	250	216	73	333	31	780
Total	2389	2063	610	399	1177	936

1 – WTP concentrations based on two LAW melters operating simultaneously.
2 – Values represent intended target concentration, test to be completed by June 2003.
NM – not measured

Test Organic	LAW Melter Feed Concentration, mg/min				HLW Melter Feed Concentration, mg/min	
	DM 1200			WTP	DM 1200[1]	WTP
	C1	A1	B1			
Chlorobenzene	1451	1451	490	1010	531	328
Trichloroethylene	1929	1929	649	1010	703	328
Naphthalene	395	395	154	10190	46	3280
Total	3775	3775	2193	12210	1280	3936

1 – Values represent intended target concentration, test to be conducted by June 2003.

The LAW feed concentrations of organics (given as mg/L) tested in the DM1200 are significantly higher than what would be required for the WTP performance demonstration test. During the LAW C1 test, the feeding period of the organic spike solution was 58 hours. This period of operation produced over three melter tank volumes of glass (~5200 kg). The LAW A1 tests had two distinct periods of melter feeding. Organic solution was fed to the DM1200 for periods of 41 hours and 23 hours. The 41-h period produced approximately 4,100kg of glass which equates to 2.4 melter turnovers. Because the melters behave as well-mixed tanks, three turnovers results in ~95% conversion of the contents of the tank. WTP R&T experience is that the redox state of the glass responds more quickly than the feed periods tested as described above often approaching equilibrium about twice as fast. Therefore, there is a sound technical basis to expect any effect of the organics on the redox state of the glass to have manifested itself within the period when organics were fed to the melter.

No divalent iron was detected in glass samples taken near the end of the LAW A1 and C1 test segments when the organic spike was fed (References 4 and 5). These results are consistent with LAW testing in general, which shows that LAW feeds with target quantities of sugar and waste Total Organic Carbon (TOC) result in fully oxidized glasses. The method detection limit is 0.8% for divalent iron. An appreciable fraction of the organic spike compounds exit the melter without reacting based on the low DRE measured for two LAW tests (see table below). This contributes to the weak affect of the spike organics on the glass redox condition. This conclusion is based on the fact the melter DREs for LAW envelope A and C tests were measured to be,

	Envelope	Chlorobenzene	Trichloroethylene	Naphthalene
Melter % DRE	LAW C1	42 %	53 %	57 %
	LAW A1	0 %	20 %	33 %

To put into perspective the incremental increase in the amount of carbon that would be added to LAW and HLW feeds during performance testing; the following table presents the g/L of carbon in the LAW melter feeds. The incremental increases in carbon of less than 7% as VOC/SVOC are not sufficient to affect the redox state of the LAW glasses.

Carbon Source	LAW A1, grams (g) carbon/L	LAW B1, g carbon/L	LAW C1, g carbon/L
Sucrose	20.9	7.2	1.8
Waste TOC	4	0.8	14
VOC/SVOC	0.9	0.3	1.0

The HLW flowsheet contains trace amounts of TOC. In addition, the use of sugar will vary depending on sludge washing efficiency in pretreatment. The concentrations of TOC, nitrates, and nitrites will dictate if and how much sugar will be required to maintain a suitable glass redox condition. HLW flowsheet testing is currently underway in 2003 to measure the rate of change of the glass redox with increasing concentrations of sugar. To date, sugar concentrations up to 25 g/L sugar (10.5 g/L carbon equivalent) have resulted in acceptable levels of reduced iron in the glass. A future DM1200 HLW test is planned to measure organic DRE in the thermal catalytic oxidation unit. This test will be performed with concentrations of total organics that are only slightly higher than projected for WTP HLW performance testing requirements. The estimated WTP HLW melter feed concentration of test organics would result in approximately 0.8 g/L carbon equivalent. This value is significantly lower than carbon levels tested using sugar. This low carbon concentration combined with the fact that the test organics do not persist in the cold cap to the extent sugar does allows us to conclude that the HLW melter would not be at risk by a performance demonstration test.

Summary

Data produced since early 2002 provides credible evidence that organic DRE performance testing of VOC and SVOC organics at levels required to determine DRE attainment at the end of the off-gas treatment train will not risk the performance life of the HLW and LAW melters.

This determination is based on the following facts:

1. The use of a limited number of hard-to-destruct representative organics is an acceptable

strategy for demonstrating DRE performance at the end of the off-gas treatment train.
2. The VOC and SVOC test organics to not persist in the cold cap, but rather evaporate or decompose at lower temperatures; thereby reducing their potential effect on the melt pool and melter components.
3. For LAW envelopes, the concentrations do not significantly increase the total carbon content in the feed such that over-reduction of the glass will occur.
4. For HLW, the concentrations are below the levels determined to be required to increase the redox state of the glass to the level that reduction of metals and sulfides have been known to occur.

References

1. WA7890008967, Hanford Facility Resource Conservation and Recovery Act Permit, Dangerous Waste Portion, Chapter 10 and Attachment 51, "Waste Treatment and Immobilization Plant."

2. Evaluation of Ecology's Expectations for the Waste Treatment and Immobilization Plant Melters and Off-Gas System Performance Requirements, 24590-WTP-RPT-ENV-02-002 Rev. 1, S. Hill, et al. River Protection Project, Waste Treatment Plant, 3000 George Washington Way, Richland, WA 99352, February 13, 2002.

3. Calculation: HLW and LAW Offgas Systems VOC Spiking, 24590-WTP-M4C-LOP-00001 Rev. 0A, E. Berrios, River Protection Project, Waste Treatment Plant, 3000 George Washington Way, Richland, WA 99352, February 7, 2003.

4. Integrated Off-Gas System Tests on the DM1200 Melter with RPP-WTP LAW Sub-Envelope A1 Simulants, VSL-02R8800-2 Rev. 0 (In Review), K.S. Matlack, et al., Vitreous State Laboratory, The Catholic University of America, Washington, DC 20064, September 3, 2002.

5. Integrated Off-Gas System Tests on the DM1200 Melter with RPP-WTP LAW Sub-Envelope C1 Simulants VSL-02R8800-1 Rev. O (In Review), K.S. Matlack, et al., Vitreous State Laboratory, The Catholic University of America, Washington, DC 20064, July 25, 2002.

6. Integrated Off-Gas System Tests on the DM1200 Melter with RPP-WTP LAW Sub-Envelope B1 Simulants VSL-03R3851-1 Rev. A (In Review), K.S. Matlack, et al., Vitreous State Laboratory, The Catholic University of America, Washington, DC 20064, May 2, 2003.

7. The Merck Index of Chemicals and Drugs, 6th Edition, 1952, Merck & Co. Rahway, New Jersey.

Hanford Facility RCRA Permit Modifications

Part III, Chapter 10 and Attachment 51

Waste Treatment and Immobilization Plant

July 11., 2003

Replacement Sections

III.10.C.14. Reserved.

(note: condition being deleted, no replacement section included)